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PTO 2003-730

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Date logged in: 11-14-02
PTO estimated words: 2618
Number of pages: 16
In-House Translation Available: _____
In-House: _____ Contractor: _____
Translator: _____ Name: Es
Assigned: _____ Priority: 2
Returned: _____ Sent: 11-20-02
Returned: 11-29-02

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PTO 03-0730

CY=DE DATE=19980129 KIND=A1
PN=196 30 073*

SYSTEM FOR THE STORAGE OF HEAT OR COLD
IN A COMPOSITE STORAGE MATERIAL CONSISTING
OF PRESSED, EXPANDED GRAPHITE AND A SOLID-LIQUID
PHASE-CHANGE MATERIAL

[System zur Speicherung von Wärme oder Kälte
in einem Speicherverbund aus
gepresstem Graphitexpandat und einem fest-flüssig
Phasenwechselmaterial]

Peter Satzger, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D. C. November 2002

Translated by: FLS, Inc.

PUBLICATION COUNTRY (10): DE
 DOCUMENT NUMBER (11): 19630073
 DOCUMENT KIND (12): A1
 (13): OFFENLEGUNGSSCHRIFT
 PUBLICATION DATE (43): 19980129
 PUBLICATION DATE (45):
 APPLICATION NUMBER (21): 19630073.8
 APPLICATION DATE (22): 19960729
 ADDITION TO (61):
 INTERNATIONAL CLASSIFICATION (51): C09K 5/06, F28D 20/02
 DOMESTIC CLASSIFICATION (52):
 PRIORITY COUNTRY (33):
 PRIORITY NUMBER (31):
 PRIORITY DATE (32):
 INVENTORS (72): SATZGER, PETER; ESKA, BENEDIKT
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 ENERGIEFORSCHUNG e.V.
 TITLE (54):
 SYSTEM FOR THE STORAGE OF HEAT OR COLD IN A COMPOSITE STORAGE
 MATERIAL CONSISTING OF PRESSED, EXPANDED GRAPHITE AND A SOLID-
 LIQUID PHASE-CHANGE MATERIAL
 FOREIGN TITLE (54A):
 SYSTEM ZUR SPEICHERUNG VON WÄRME UND KÄLTE IN EINEM
 SPEICHERVERBUND AUS GEPRESSTEM GRAPHITEXPANDAT UND EINEM FEST-
 FLÜSSIG PHASENWECHSELMATERIAL

The invention concerns a system consisting of pressed, expanded graphite and a solid-liquid phase-change material for the storage of heat or cold in a composite storage material.

The technology of the storage of thermal energy is important, because energy can be saved on the one hand by the temporal decoupling the energy supply and demand and, on the other, economic advantages can be achieved. Moreover, the application of periodically available energy sources such as, for example, solar energy, is enabled. It is known that phase changes with a heat shading can also be employed together with chemical reactions for the storage of heat or cold. Very frequently, substances with a solid-liquid phase change - for the most part also designated as PCM (phase-change material) - are proposed, thus, for example, water for the storage of cold. But solid-gaseous phase changes can also be used, for example, gas-solid reactions.

Arising with all these thermal energy-storing possibilities are one or more of the following technical difficulties, which must be overcome:

changes in volume during the phase change, supercooling, separation

*Numbers in the margin indicate pagination in the foreign text.

of the components, agglomeration, low thermal conductivity, expensive heat-exchanger requirements.

The gas-solid reactions additionally require that the solid reactor, in which the gas reacts with the solid substance, will have a high gas permeability. For gas-solid reactions, a matrix consisting of pressed, expanded graphite was proposed as a carrier material for the solid substance (US-patent 4,852,645). The reactive solid substance, mixed with expanded graphite, is pressed for that purpose to form a reaction composite. This inert graphite matrix is elastic and can thus, up to a certain degree, absorb the swelling of the reactive solid substance. Moreover, it has a high thermal conductivity and high gas permeability as a result of the high porosity of up to 90%.

When there is a great reduction in porosity due to a high loading of the matrix with reactive solid substance, a correspondingly greater degree of swelling must be absorbed by the graphite matrix. If the loading becomes too large, corresponding to a reduction in porosity to less than 60%, the graphite matrix will be damaged by the swelling taking place during the reaction, and the properties of the matrix, such as high gas permeability and good thermal conductivity, will thus be greatly impaired. The application of the graphite matrix is thus limited by the capacity

of the matrix to absorb swelling.

It is known, moreover, that PCMs for solid-liquid phase changes can be incorporated into matrices consisting of various materials. It was thus proposed, for example, that PCM be built into an unhardened polymer matrix as a reservoir (US patent 4,003,426). As indicated in the patent, this method is however usable only in the case of storage materials for thermal energy, which yield stable dispersions with the unhardened polymer - which is only possible for very few materials.

The application of a graphite matrix for the cold/heat storage with PCM was thus far not possible for two reasons:

1. A high loading of the inert graphite matrix with a reactive solid substance, so that the porosity of the storage composite will lie below 60%, as is necessary for a reservoir with PCM in order to achieve a high energy density, had negative effects during gas-solid reactions upon the porosity, gas permeability and elasticity. It was for this reason anticipated that the graphite matrix would be destroyed by the change in volume during the phase change of a PCM.

2. Charges that produce a residual porosity of the composite of less than 40% were not possible with existing production methods.

The addresses the problem of developing a composite for heat- or cold-storage and its production, which is characterized by the fact that a PCM is embedded in a suitable matrix that possesses the following properties:

- sufficiently high mechanical stability
- sufficient expansion tolerance
- activity as a nucleating agent, in order to reduce supercooling
- be economically, ecologically and easily producible

It was determined, surprisingly, that a stable composite can be achieved with a volumetric weight of the graphite matrix of more than 75 g/I as a starting point, despite the swelling of the PCM, if the loading with PCM is restricted according to the invention to preferably 90% of the pore volume available. A residual porosity of about 10% thus remains.

A method permitting such high loading was found according to the invention, which is characterized by the fact that, prior to impregnation, the matrix produced from pressed, expanded graphite is preferably evacuated at a pressure of 10^{-2} mbar, and the PCM for subsequent impregnation is heated to temperatures preferably between 10 and 40 K above the melting point, but maximally to the evaporation temperature of the PCM. The impregnating device is

seen in **Fig. 1**. By opening the valve to the PCM container, the melted PCM, then present in excess, is sucked into the graphite matrix. Then, the storage composite is preferably cooled to a temperature below room temperature, to reduce an outgassing of the PCM until the storage container is closed.

Most of the proposed applications for PCMs lie within the temperature range of from -25 to 150°C. It is usually difficult of course to prepare a storage composite suitable for a specific application. Thus, as described above, the selection of possible /3 PCMs for the polymer matrix is quite limited. On the other hand, the graphite matrix is not subject to these limitations, the designing of a reservoir being greatly simplified as a result.

Due to the described restriction of the loading of the matrix with the PCM to preferably 90%, the result, as shown by **Fig. 2**, is that the pores in the matrix are only partially filled. The graphite matrix is distinguished by an anisotropy both in the structure as well as in the elasticity. An expansion of the pores perpendicular to the preferred direction of the graphite layers is thus possible at the expense of other pores that are either not or only partly filled. Thereby resulting is a great tolerance of the matrix with regard to an expansion of the PCM.

Arising due to this high elasticity of the storage composite is a great advantage for application: If the elasticity is so great that the swelling of the PCM (for example, water/ice: 8%) can be absorbed by the composite completely internally, as it is the case for this invention, it will be possible, in contrast to the at present commercially available for the storage of cold, to eliminate expensive adjustment technology for preventing complete crystallization, because even a complete crystallization of the reservoir will not lead to the destruction of the reservoir or the reservoir container.

Furthermore, supercooling for the formation of crystal nuclei, viewed as critical but necessary in the case of PCMs, can be greatly reduced by this new storage composite. As a result, a higher temperature can be achieved or set during the liberation of heat from the reservoir, which means, in the case of a cold reservoir, a lower required cold output for loading and, for a heat reservoir, a higher useful temperature. In contrast to most of the proposed additions proposed as nucleating agents for phase change, the pure PCM can be used in this matrix. Unmixing, like that often taking place with the addition of nucleating agents, is therefore not possible.

Examples

The following examples 1 to 4 show experiments with water as the PCM. Water has many advantages as an agent for storing cold, such as in particular a high storage density, but two great disadvantages, namely, a volume increase of 8% during the phase change from liquid to solid and a necessary supercooling of about 10 K for this phase change. For that reason, its use in small, compact reservoirs for cold was thus far very difficult. As the following examples show, both disadvantages can be avoided or considerably mitigated by the invention.

Example 1

Expanded graphite with a bulk density of 2 g/l was pressed into cylindrical tablets (diameter: 42 mm), with volumetric weights, i.e. mass per unit of volume, of from 36 g/l to 122 g/l. The tablets were evacuated to a pressure of $3 \cdot 10^{-2}$ mbar and then filled with the PCM - distilled water - to achieve an average loading with water corresponding to a water volumetric weight of 660 g/l.

The composite articles were frozen at -23°C and then thawed again. It was found that storage composites with a graphite volumetric weight of up to 75 g/l were destroyed by the freezing process. On the other hand, storage composites with volumetric

weights of more than 75 g/l remained stable. Moreover, no negative influence upon the stability of the graphite matrix could be detected after several complete charging/discharging cycles of the reservoir.

Example 2

Several pressed tablets were produced in analogy to Example 1, but the volumetric weight of the graphite was 100 g/l, the water loading being seen in Table 1, along with the pressures applied to the tablets in the axial direction.

The storage composites were respectively frozen at -23°C and their dimensions then compared with their original dimensions. The parameters and the results are summarized in Table 1:

Volume-expansion data

After impregnation		Loading/ Excess pressure bars	Expansion	
Volumetric wt. of water, g/l	Porosity %		Radial %	Axial %
600	35.5	0	< 0.5	4
700	26	0	< 0.5	4
600	35.5	0.1	< 0.5	1.5
700	26	0.1	< 0.5	1.5
700	26	1	< 0.5	< 0.5
800	15.5	1	< 0.5	< 0.5
1,000	0	0		8

In the case of external axial pressures of 1 bar, no further axial expansion could be measured. It was thus confirmed that the

expansion of the PCM's water (pure: 8%) can be completely compensated by the graphite matrix in the presence of a sufficiently large, technically easily implemented, external pressure.

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Example 3

A cylindrical storage composite was produced with a graphite volumetric weight of 100 g/l and a water volumetric weight of 900 g/l.

This composite was inserted in a stainless-steel tube closed with two stainless-steel end caps, through which two NiCr-Ni thermal elements were led, one in the middle of the cylinder and one at half the cylinder radius. The stainless-steel container is placed in a thermal bath and can be submitted to defined cooling. If the supercooling temperature required for crystal formation on the thermal element is achieved, the temperature on the thermal element will jump from the supercooling temperature to the actual freezing temperature of water, 0°C. A required supercooling of about 5.5 K was detected. The necessary supercooling for water was measured at 9.9 K by a reference measurement on water with no graphite matrix. By using the matrix, a reduction of supercooling by approximately half was achieved.

Example 4

An expanded graphite with a bulk density of 2 g/l was pressed into tablets with a volumetric weight of 100 g/l. After the evacuation of these tablets to less than 10^{-2} mbar, these tablets were impregnated with a saturated, aqueous magnesium acetate solution. In Example 1, the solution with room temperature was added. A volumetric weight of the solution of 450 g/l was achieved. On the other hand, in Example 2, the solution was heated to 36°C. A volumetric weight of the solution in the storage composite of 683 g/l was then achieved.

Parts of the process/system are shown in **Fig. 1** and **Fig. 2** for the purpose of explanation.

Fig. 1 shows, schematically, a device for the impregnation of graphite matrices with PCM. The graphite matrix is thereby evacuated in a container and then saturated with liquid PCM under a vacuum.

Fig. 2 shows, schematically, the structure of the storage composite (lateral section). Visible is the porous graphite matrix with PCM and gas/vapor inclusions.

Patent Claims

1. Process/system for the storage of heat or cold with the aid of the phase change of a material (PCM), **characterized by the**

fact that the solid/liquid PCM is present in a matrix consisting of pressed, expanded graphite.

2. Process/system according to Claim 1, characterized by the fact that the volumetric weight of the graphite matrix amounts to 75-1,500 g/l without PCM, and sufficient PCM is inserted in the matrix to achieve a residual porosity of 2-60% in the storage composite.

3. Process/system according to Claim 1, characterized by the fact that volumetric weight of the graphite matrix amounts to 75-300 g/l without PCM, and sufficient PCM is inserted in the matrix to achieve a residual porosity of 5-30% in the storage composite.

4. Process/system according to at least one of the Claims 1 to 3, characterized by the fact that the PCM is introduced in liquid form, by vacuum impregnation, into a matrix that is produced by pressing expanded graphite, in which case the matrix is evacuated to a pressure of less than 10 mbar before impregnation.

5. Process/system according to at least one of the Claims 1 to 4, characterized by the fact that the PCM is introduced in liquid form, by vacuum impregnation, into a matrix that is produced by pressing expanded graphite, in which case the matrix is evacuated to a pressure of less than 10^{-2} mbar before impregnation.

6. Process/system according to at least one of the Claims 1 to 5, characterized by the fact that the PCM is heated, before impregnation, to a temperature above the melting temperature, up to maximally the evaporation temperature of the PCM.

7. Process/system according to at least one of the Claims 1 to 6, characterized by the fact that the matrix is heated, before impregnation, up to maximally the evaporation temperature of the PCM.

8. Process/system according to at least one of the Claims 1 to 7, characterized by the fact that the composite is cooled to room temperature immediately after impregnation, but maximally down to the melting temperature of the PCM.

9. Process/system according to at least one of the Claims 1 to 8, characterized by the fact that the PCM has a solid/liquid phase change in the temperature range of from -25°C to 150°C .

10. Process/system according to at least one of the Claims 1 to 8, characterized by the fact that the PCM is water.

11. Process/system according to at least one of the Claims 1 to 8, characterized by the fact that the PCM consists of a mixture with eutectic or congruent melting characteristics, consisting of one or more of the following components:

CaBr ₂	NaCl	Al(NO ₃) ₂
CaCl ₂ ·6H ₂ O	NaF	Ca(NO ₃) ₂
CaCl ₂	NaOH	Cd(NO ₃) ₂
KF	NaOH·3.5H ₂ O	Co(NO ₃) ₂
Kcl	Na ₂ HPO ₄	KNO ₃
KF·4H ₂ O	Na ₂ SO ₄	LiNO ₃
LiClO ₃ ·3H ₂ O	Na ₂ SO ₄ ·10H ₂ O	Mg(NO ₃) ₂
Mg ₂ SO ₄	NH ₄ Cl	NaNO ₃
MgCl	NH ₄ H ₂ PO ₄	Ni(NO ₃) ₂
ZnCl ₂ ·2.5H ₂ O	NH ₄ CO ₃	Zn(NO ₃) ₂
ZnSO ₄	NH ₄ NO ₃	Zn(NO ₃) ₂ ·6H ₂ O
Ba(OH) ₂	NH ₄ F	Cu(NO ₃) ₂
H ₂ O	(NH ₄) ₂ SO ₄	acetic acid
SO ₃ ·2H ₂ O		acetate

12. Process/system according to at least one of the Claims 1 to 8, characterized by the fact that PCM consists of a mixture with eutectic or congruent melting characteristics, consisting of one or more of the following components:

paraffins, fatty acids, oligomers, glycols, alcohols, caprylic acid.

13. Process/system according to at least one of the Claims 1 to 8, characterized by the fact is a clathrate-forming substance.

2 Page(s) of drawings attached

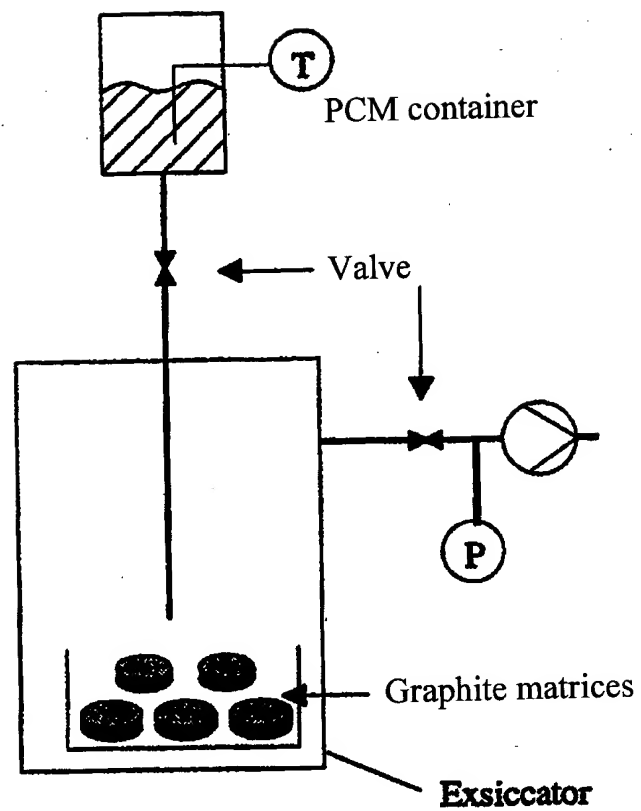


Figure 1

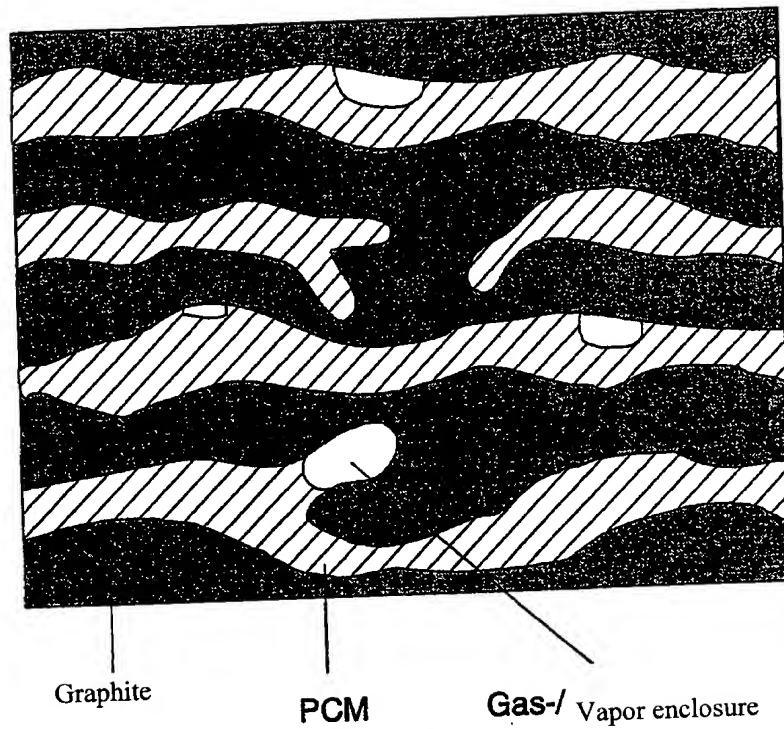


Figure 2